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13. ABSTRACT *(Maximum 200 words)*

This research aims to develop sensors and devices based on polymer gels. Under the support of the ARO grants (Technical monitor: Dr. Douglas Kiserow, Grant No. DAAH04-93-G-0215), we have made significant progress toward understanding, synthesis and application of gel systems. The major inventions are: (1) Synthesis and application of modulated polymer gels, (2) Bending of N-isopropylacrylamide gel under influence of infrared light, (3) CO_2 laser controlled transmission of visible light in N-isopropylacrylamide gel, (4) Shape memory gels have been synthesized based on spatial modulation of the chemical nature of gels. A variety of shapes have been obtained including "spiral", "fish", "numbers", "alphabets" and "tube", and (5) Change of the ultrasonic attenuation near the volume phase transition of gels. The accomplishments for the past four years have been published in 16 papers including one in Science, four in Journal of Chemical Physics, three in macromolecules, and two in Journal of Applied Polymer Science. Some of the results have been reported by ***Chemical and Engineering News*** (June 9, p.36-37, 1997), and ***Chemistry & Industry*** (July 15, p. 531-532,1996). One patent was filed to the U. S. Patent Office. Two graduate students have obtained their Ph.D. under the support of the ARO grants.

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(1) List of manuscripts published under ARO sponsorship

1. Y. Li, C. Li, and Z. Hu, "Pattern formation of constrained acrylamide/sodium acrylate copolymer gels in acetone/water mixture," J. Chem. Phys. **100**, 4637 (1994).
2. C. Li, Z. Hu, and Y. Li, "Temperature and time dependence of patterns of surface patterns in constrained ionic N-isopropylacrylamide gels," J. Chem. Phys. **100**, 4645 (1994).
3. Y. Li, C. Li, and Z. Hu, "Ratio of moduli of polyelectrolyte gel in water with and without salt," *Superabsorbent Polymers,* Amer. Chem. Soc. Symposium Series **573**, Edited by F.L. Buchholz and N.A. Peppas, Chapter 5, 64 (1994).
4. X. Zhang, Y. Li, Z. Hu, C. Li, and C. L. Littler, "Infrared-light induced volume phase transition in N-isopropylacrylamide gel", Proceedings of Second International Conference on Intelligent Materials, Edited by C.A. Rogers and G.G. Wallace, 1341 (1994).
5. X. Zhang, Y. Li, Z. Hu, and C. L. Littler, "Bending of N-isopropylacrylamide gel under influence of infrared light," J. Chem. Phys. **102**, 551 (1995).
6. Z. Hu, Y. Li, X. Zhang, and C. L. Littler, "CO_2 laser controlled transmission of visible light in N-isopropylacrylamide gel," Polymer Gels and Networks **3**, 267 (1995).
7. Y. Li, Z. Hu, X. Zhang, and C. L. Littler, "Effect of infrared irradiation on polymer gels," Mater. Sci. & Eng.: **C2**, 221 (1995).
8. Y. Li, G. Wang, and Z. Hu, "Turbidity study of spinodal decomposition of N-isopropylacrylamide gels," Macromolecules **28**, 4194 (1995).
9. Z. Hu, X. Zhang, and Y. Li, "Synthesis and application of modulated polymer gels," Science **269**, 525 (1995).
10. Z. Hu, Y. Li, X. Zhang and Y. Chen, "Bending and shape memory effects of gels with modulated structures," in *Smart Structures and Materials 1996: Smart Materials Technologies and Biomimetics*, A. Crowson, Editor, Proc. SPIE 2716, 224 (1996).
11. X. Zhang, Z. Hu, and Y. Li, "Bending of bi-gels," J. Chem. Phys. **105**, 3794 (1996)
12. Y. Li, Z. Hu, and Y. Chen, "Shape memory gels made by the modulated gel technology," J. Appl. Polym. Sci. **63**, 1173 (1997).
13. X. Zhang, Z. Hu, and Y. Li, " The phase transition and shear modulus of ionic N-isopropylacrylamide gels in concentrated salt solutions," J. Appl. Polym. Sci. **63**, 1851 (1997).
14. C. Wang, Y. Li and Z. Hu, "Swelling kinetics of polymer gels," Macromolecules **30**, 4727 (1997).
15. X. Zhang, Z. Hu, and Y. Li, "Rubber elasticity of acrylamide gels in high network concentration." Polymer. (in press).
16. C. Li, Z. Hu, and Y. Li, "Acoustic attenuation of N-isopropyacrylamide gel near the volume phase transition," To be submitted to Macromolecules in two weeks.

(2) Scientific personnel supported by this project

- Principal Investigator: Zhibing Hu
- The students who obtained their Ph. D under ARO support:
  C. Li, Ph. D. Dissertation, 1994, entitle "Scaling behaviors and mechanical properties of polymer gels". Dr. Li is now a Post-Doctoral Research Associate at University of Illinois at Urbana-Champaign.
  X. Zhang, Ph. D. Dissertation, 1996, entitle "Synthesis and physical properties of environmentally responsive polymer gels". Dr. Zhang is now employed as a Senior Research Scientist at Kimberly-Clark Corporation, Neenah, Wisconsin.

(3) Report of Invention

- Synthesis and application of modulated polymer gels

- Bending of N-isopropylacrylamide gel under influence of infrared light
- CO_2 laser controlled transmission of visible light in N-isopropylacrylamide gel
- Shape memory gels have been synthesized based on spatial modulation of the chemical nature of gels. A variety of shapes have been obtained including "spiral", "fish", "numbers", "alphabets" and "tube".
- Change of the ultrasonic attenuation near the volume phase transition of gels

(4) Scientific progress and accomplishments

The major accomplishments have been published in 16 papers. The condensed abstracts of some representative papers are given below.

- **Pattern formation of constrained acrylamide/sodium acrylate copolymer gels in acetone/water mixture, J. of Chemical Physics 100**, 4637 (1994).

Pattern formation and evolution in constrained acrylamide/sodium acrylate (PAAM/SA) gels have been investigated in acetone/water mixture. The constraint is achieved by crosslinking the gel slabs onto a rigid substrate. Depending on the solvent composition and ionic strength of the sample, different patterns, i.e., hexagonal, grains, and bubbles, have been observed. These patterns are formed at acetone concentration, below, near and above the concentration at which the gel volume phase transition occurs. The wavelengths of hexagonal and bubble patterns are found to be the same while that of the grain pattern is four times smaller. It is suggested that the shrinking patterns are formed due to the dense gel surface produced during the shrinking process.

- **Temperature and time dependence of surface patterns in constrained ionic N-isopropylacrylamide gels, J. of Chemical Physics 100**, 4645 (1994).

Surface patterns in ionic N-isopropylacrylamide (NIPA) gels have been investigated under external constraint. Hexagonal, grain and bubble patterns have been observed at temperatures below, near, and above the phase transition temperature T_C. It is found that the behavior of these patterns depends not only on temperature, time and external constraint, but also on the thermal path. The experiments show that each hexagonal cell evolves into a bubble for NIPA gels, while a bubble can be present in the middle of a hexagonal cell for acrylamide gels.

- **Infrared-Light Induced Volume Phase Transition in the N-isopropylacrylamide gel Proceedings of Second International Conf. on Intelligent Materials, 1341 (1994).**

The volume phase transition in the N-isopropylacrylamide (NIPA) gel has been investigated under the irradiation of an infrared laser light. The volume of gel shrinks upon increasing the laser power. The temperature, recorded simultaneously with the laser power, indicates that the volume transition of the gel is caused by direct heating from the laser. This heating also results in an osmotic pressure difference between the front surface area of the gel and the rest part of the gel, and causes the gel to bend. The bending effect has been studied as a function of time with and without laser irradiation. This experiment shows the feasibility of the development of optical gel sensors and devices

- **X. Zhang, Y. Li, Z. Hu, and C. L. Littler, "Bending of N-isopropylacrylamide gel under influence of infrared light," J. Chem. Phys. 102**, 551 (1995).

A CO_2 infrared laser has been used to irradiate a straight cylindrical N-isopropylacrylamide (NIPA) gel. It is found that the infrared laser not only induces the volume phase transition in the gel, but also causes the gel to bend toward the laser beam. When the laser is blocked, the gel becomes straight again. The transition between the straight and the bending gel is fully reversible. The maximum bending of the gel is

comparable to that obtained for poly(vinyl alcohol)-poly(sodium acrylate) copolymer gel under the influence of an electric field. The bending effect has been systematically studied as a function of CO_2 laser power, time, and the sample cell temperature.

- **Z. Hu, Y. Li, X. Zhang, and C. L. Littler, "CO_2 laser controlled transmission of visible light in N-isopropylacrylamide gel," Polymer Gels and Networks 3**, 267 (1995).

The transmission of visible laser light through the N-isopropylacrylamide (NIPA) gel has been measured under the influence of an applied co-axial CO_2 infrared laser beam. It is found that the transmission can be controlled by adjusting the infrared laser power. The change of transmission of the visible light as the infrared laser is turned on is completely reversible. The response time required for the change of the transmission is much faster than that required for the change of gel volume. Since the response time is short, the sample cell temperature remains almost constant during the infrared laser on-and-off cycles. The experimental results have been explained in terms of spinodal decomposition theory.

- **Y. Li, G. Wang, and Z. Hu, "Turbidity study of spinodal decomposition of N-isopropylacrylamide gels," Macromolecules 28**, 4194, (1995).

The kinetics of the spinodal decomposition of the volume phase transition of N-isopropylacrylamide gel is studied using a turbidity technique. Three stages were identified: the early stage, the transition stage, and the frozen stage. The early stage can be explained by Cahn-Hilliard-Cook's theory. In the transition stage, the cascading network segment association process causes the turbidity to increase faster than the early stage. The transition stage is characterized by its turbidity growth peak. The final stage, the frozen stage, is characterized by the high turbidity and vanishing turbidity growth rate.

- **Z. Hu, X. Zhang, and Y. Li, "Synthesis and application of modulated polymer gels" Science 269**, 525 (1995).

A new class of environmentally responsive materials based on spatial modulation of the chemical nature of gels has been proposed and demonstrated. The modulation is achieved by interpenetrating only part of one gel network with another gel network. Therefore, these gels have an internally heterogeneous, or modulated, structure. Three simple applications based on the modulated gels are presented: a bi-gel strip, a shape memory gel, and a gel hand. The bi-gel strip bends almost to a circle when its temperature or solvent is changed. The shape memory gel changes its shape from a straight line to a pentagon, to a quadrangle at different temperatures. The gel hand in water can grasp or release an object simply by adjusting its temperature.

- **X. Zhang, Z. Hu, and Y. Li, "Bending of bi-gels," J. Chem. Phys. 105, 3794 (1996)**

The bending of bi-gels has been studied as a function of temperature, acetone concentration, and NaCl concentration. The bending mechanism of the bi-gels reported here is due to the engineered structure heterogeneity, in contrast with previous homogeneous gel bending which is induced by external gradient fields. A theoretical model is used to estimate the collective diffusion coefficient D_c.

- **Y. Li, Z. Hu, and Y. Chen, "Shape memory gels made by the modulated gel technology," J. Appl. Polym. Sci. 63, 1173 (1997).**

Shape memory gels based on interpenetrating only part of one gel network with another gel network have been synthesized. These gels consist of two parts: a control element which is responsive to a designated environmental stimuli, and a non-responsive substrate element. By designing the pattern in the

gelation process, a variety of shapes are obtained including "spiral", "fish", "numbers", "alphabets" and "tube". The change between two different shapes can be controlled by external stimuli and is reversible.

- **X. Zhang, Z. Hu, and Y. Li, " The phase transition and shear modulus of ionic N-isopropylacrylamide gels in concentrated salt solutions," J. Appl. Polym. Sci. 63, 1851 (1997).**

Swelling and mechanical properties of thermally sensitive N-isopropylacrylamide (NIPA) hydrogels containing 0-35 mM sodium acrylate (SA) comonomer have been investigated at room temperature. As the NaCl concentration increases the ionic NIPA gels shrink. In a dilute sodium chloride solution with N_aCl less than 0.1 M the conformational change of the gels is a simple process of osmotic deswelling. As sodium chloride concentration increases greater than 0.8 M the gels undergo a shrinkage phase transition.

- **C. Wang, Y. Li and Z. Hu, "Swelling kinetics of polymer gels," Macromolecules 30, 4727 (1997).**

The kinetics of gel swelling has been theoretically analyzed by considering coupled motions of both the solvent and the polymer network. The solvent motion patterns for a long cylindrical gel and a large disk gel have been obtained. The previous network swelling results by Li and Tanaka (L-T) can be derived from the current model without using the two imaginary processes approaches.

- **X. Zhang, Z. Hu, and Y. Li, "Rubber elasticity of acrylamide gels in high network concentration." Polymer. (in press).**

Shear modulus of polyacrylamide (PAAM) gels has been measured with the network concentration ranging from 0.02 to 1.0 g/cm^3. In the low concentration region, the shear modulus is a scaling function of network concentration with the exponent equal to 1/3, which is expected by classical rubber elasticity theory. As the concentration increases, the behavior of shear modulus deviates the scaling law significantly. The modified Mooney theory which incorporated a second higher order term is used to explain the results. The measured shear modulus data can be fitted well with the new theory, with two exponents equal to 0.33 and around 2.0 to 2.5, respectively.

- **C. Li, Z. Hu, and Y. Li, "Acoustic attenuation of N-isopropyacrylamide gel near the volume phase transition," To be submitted to Macromolecules.**

The acoustic attenuation of the longitudinal wave in N-isopropylacrylamide (NIPA) gel in water has been measured as a function of temperature in the frequency range from 5 MHz to 30 MHz. Associated with the volume phase transition at the temperature T_c, the attenuation exhibits a sharp peak. As the ultrasonic frequency increases, the attenuation peak increases and shifts to higher temperatures. The critical behavior of the attenuation in the swollen phase near the critical phase transition has been analyzed in terms of a dynamic-scaling theory. The data collapse reasonably onto a scaling function as the theory predicted with the scaling exponent zv=1.93.

(5) Technology Transfer

- Z. Hu, X. Zhang and Y. Li, "Synthesis and uses of heterogeneous polymer gels," The intention of filing a patent was submitted to U. S. Patent Office in 1995. The U. S. patent was formally filed in December, 1996 through Kimberly-Clark Corporation.